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Field Experience in Sampling Hazardous Waste Incinerators

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Field Experience In Sampling Hazardous Waste Incinerators

by

Paul Gorman[1]
Fred Bergman[1]
Don Oberacker[2]

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INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

1 Midwest Research Institute
425 Volker Boulevard
Kansas City, Missouri 64110

2 U. S. Environmental Protection Agency
Industrial Environmental Research
Laboratory-Cincinnati
Incineration Research Group
26 West St. Clair Street
Cincinnati, Ohio 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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16. ABSTRACT

This paper is for presentation at the 77th annual meeting of the Air Pollution Control Association, June 24-29, 1984. The paper contains much useful, pragmatic information gained through numerous hazardous waste incinerator trial burn-type investigations performed for EPA by the contractor (MRI). Included are normal preparations for sampling points, waste inventory arrangements for performing the tests, and practical considerations for using standard EPA stack sampling techniques, etc. which may otherwise be overlooked by new or unfamiliar contractors conducting future incinerator trial burn sampling.

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Introduction

The Resource Conservation and Recovery Act (RCRA) has resulted in several hazardous waste regulations applicable to incinerators, including where appropriate, requirements for trial burns as part of the permitting procedures. During the period 1981-1983, Midwest Research Institute (MRI) has conducted trial burn tests for both EPA and industry at twelve hazardous waste incinerators. These tests are the basis for this paper on field experience in sampling hazardous waste incinerators. While sampling and analysis are equally important, this paper focuses on the important aspects of the sampling activity and experience, including problems that were encountered. Material presented is directed to the preparation for, and conduct of, the field sampling activities; analysis aspects are not addressed because their complexity exceeds the scope of this paper.

Trial burn measurements have four primary purposes:

1. Determination of destruction and removal efficiency (DRE) for each designated principal organic hazardous constituent (POHC).

2. Determination of particulate emission concentration.

3. Determination of hydrogen chloride (HCl) removal efficiency.

4. Establishing design and operating conditions that will be specified in the permit application and may become a part of the subsequent operating permit.

Since the operating conditions will (or may) be specified in an operating permit issued after the trial burn, they are usually a major concern. These conditions are a part of the subject area referred to in this paper as "process considerations," and are discussed first. Subsequent sections discuss field sampling experience, including the sampling methods used to determine DRE, particulate concentration, and HCl emission rates, etc.

Process Considerations

The tests conducted by MRI involved many different hazardous waste streams and a variety of incinerator sizes and types (e.g., rotary kiln, liquid injection, etc.) including commercial (off-site) incinerators and captive (on-site) incinerators. Discussions in this paper generally apply to both types, but some of the items discussed may be more important to one than the other.

A typical sampling and analysis plan, probably submitted as part of the trial burn plan in the RCRA Part B permit application, could look much like the one shown in Table I. The sampling and analysis plan

Table I. Typical sampling and analysis plan.

	Sampling point	No. of samples per run	Sampling method or procedures	Analysis parameters
1.	Solid waste feed	1 composite	Collect subsample every 15 min (or sample each drum)	POHCs, HHV, Cl, H_2O
2.	Aqueous feed	1 composite	Collect subsample every 15 min	POHCs, Cl
3.	Liquid organic feed	1 composite	Collect subsample every 15 min	POHCs, HHV, Cl, H_2O
4.	Venturi feed water	1 composite	Collect subsample every hour	POHCs, Cl
5.	Absorber feed water	1 composite	Collect subsample every hour	POHCs, Cl
6.	Venturi liquid effluent	1 composite	Collect subsample every hour	POHCs, Cl
7.	Absorber liquid effluent	1 composite	Collect subsample every hour	POHCs, Cl
8.	Stack effluent	1	Modified Method 5	Particulate weight, Cl^-, semivolatile POHCs
		1	VOST[a]	Volatile POHCs
		1	Integrated gas bag	Orsat for O_2 and CO_2
		Continuous	Continuous analyzers	CO, O_2, total hydrocarbons

[a] Volatile Organic Sampling Train

designates each stream to be sampled, how each will be sampled, and the frequency of sampling. Other parts of the test plan must also designate the analysis to be performed on each sample and specify the analytical methods to be used. Development of the plan requires some knowledge of the waste characteristics, including designation of the POHCs. Once the sampling and analysis plan has been developed, planning for the actual field sampling can commence. As a first step in that planning activity, there are some critical process considerations that must be addressed, as follows:

- Quantity of Waste Required
- Waste Characteristics
- Waste Feedrates
- Operating Schedule
- Design Considerations
- Allowable Process Variations

Each of these process considerations is discussed in the sections below. The order in which they are presented is arbitrary because they are all important and ignoring any one of them can have serious consequences.

Quantity of Waste Required

Adequate waste must be available for a trial burn to meet the specifications set out in the trial burn plan portion of the Part B permit application. Also, any subsequent operating permit will likely place limits on the wastes that can be burned, and these limits will be based on the characteristics of the trial burn wastes. Therefore, one of the first considerations in planning a trial burn is to ascertain that adequate quantities are available of each specific waste that is to be used in the tests. Also, each specific waste must possess certain characteristics, as is discussed in the next section.

The quantity of waste needed for the trial burn depends on the number of runs to be performed and the time required for each run. Three runs are recommended by EPA for each operating condition to be tested,[1] and the actual sampling time for each run is usually about 3 h. However, the plant must have reached steady state operating conditions for at least 1 h prior to the start of sampling, and actual sampling time may require 4 to 6 h. Thus, for three runs the plant should have waste adequate for three 8-h periods. In addition, it is preferable that the plant continue to burn the test wastes between runs (e.g., at night), which would require waste adequate for a 56-h period.

Obviously, the quantities of waste required can be rather large. For example, if a liquid injection incinerator fires at a rate of 20 Lpm (5.3 gpm), the amount required for three 8-h periods is 28,800 L (7,600 gal.). If the same wastes are burned throughout the entire test period of 56 h, as is desirable, the total quantity required is 67,200 L (17,700 gal.). Clearly, some amount of preplanning is needed to ensure that these large quantities are available and that they meet test specifications.

Waste Characteristics

If the characteristics of the waste and the POHCs have been designated in a trial burn plan, then the actual waste burned during the trial burn must possess those characteristics. For a captive facility whose waste does not vary significantly, having sufficient amounts of the correct waste available for the trial burn can probably be accomplished with little problem and without the necessity of storing an inventory of waste. On the other hand, waste received at an off-site facility can vary significantly, so some plan or method must be devised to ensure that there is sufficient waste available for the trial burn and that the waste possesses the specified characteristics. This requirement may result in a need to store waste that possesses those characteristics or to prepare a synthetic waste possessing those characteristics. Some of the most important waste characteristics that are usually specified in a trial burn plan are:

Physical properties (i.e., liquid, solid or gas)
Viscosity (minimum)
Heating value
Cl and ash content (minimum)
Specific POHCs and their concentrations

It is very important that the wastes used in the trial burn contain the compounds designated as POHCs. To ensure that the wastes contain these POHCs, synthetic mixtures may be prepared, or a mixture containing the POHCs may be continuously spiked into the waste feed stream(s) during the trial burns.

During tests at five different sites, a 50/50 mixture of carbon tetrachloride (CCl_4) and trichloroethylene (TCE) was continuously pumped (spiked) into the liquid organic waste feed line. (Both of these compounds have low heats of combustion and are considered difficult to incinerate.) The purpose of this spiking was to add the two compounds to the waste at a concentration of about 10,000 μg/g, to ensure that the waste contained adequate concentrations of both.

Results, however, indicated a problem with the spiking system. Analysis of samples taken at a point downstream of the spiking point revealed that, in some instances, the measured concentrations of CCl_4 and TCE were only one-half or one-third of the expected concentration, as calculated from the spiking rate and the waste feedrate. Investigation of this problem indicated that the most likely cause was poor mixing of the spiking solution with the waste feed. For that reason, prior to tests at a different plant, in-line mixers were installed in the waste feed line between the spiking point and the sampling point. Results showed good agreement between the concentration determined by analysis of the liquid waste feed samples and the concentration calculated from the spiking rate and waste feed rate. These results indicate that in-line mixers should be used whenever POHCs are to be continuously spiked into a waste feed line, except in cases in which the waste has a high solids content or other characteristics that could cause plugging of the mixer.

There is another very important aspect of the concentration of POHCs in the waste feeds, whether continuously spiked with the waste or prepared prior to the trial burn. Results from tests conducted by MRI and others indicate that the DRE for POHCs increases as the POHC concentration in the waste feed increases. Consequently, the likelihood of achieving the required DRE of 99.99% is increased if the concentration of POHCs in the waste feed is as high as possible (preferably 10,000 μg/g or greater). High concentrations are especially important if selected POHCs happen to be compounds that are also common products of incomplete combustion (PICs), such as benzene, toluene, naphthalene, or methylene chloride. PICs are herein defined as any compound that was detected in the stack gas which could have been designated as a POHC if it had been present in the waste feed, but that was not detected in the waste feed at a concentration above 100 μg/g.

Waste Feedrates

Determination of waste feedrates is a critical factor for calculating DRE. Tank level measurements are usually considered the most accurate method available for determining feedrates because it is usually impractical to require a true calibration of flowmeters in the field. There are cases, however, in which flowmeters would be more accurate; for example, the level change in a large tank over a test period could be quite small and therefore difficult to measure accurately. One aspect of process monitoring is to estimate the level changes that may be involved and to ascertain how the most accurate measurements can be made. Whenever possible, feed tank level changes should be obtained. In the MRI tests, liquid waste feedrates were based on measurements of feed tank levels before, during, and after each test. In most cases, the plants were equipped with feed flowmeters, so these readings were recorded and cross-checked with the feedrates determined from the tank level changes.

For most test sites, it was possible to determine liquid waste feedrates from tank level changes by using a dipstick or level gages. At one plant with a pressurized feed tank and no level gage, the feed tank was depressurized and the level measured before and after the test period.

Measurement of liquid waste feedrates is relatively simple, but that may not be true for gaseous waste feeds. Only one plant tested by MRI had a gaseous waste feed, and that feedrate had to be based on the plant's gas flowmeter. Since readouts from gas flowmeters (e.g., Nm^3/min) are usually based on a certain temperature and pressure, one must remember to correct the readings if the pressure and temperature are different from those specified in the instrument data sheet. Obtaining copies of original flowmeter data sheets, such as orifice data sheets, is sometimes quite difficult.

None of the plants tested by MRI used continuous feeding of solids, but some did include the intermittent feeding of solids in drums. Results of the preplanning activities indicated that preweighing and

numbering of all drums was the most practical method of determining the solid waste feedrate. Even then, it was still necessary to record the drum number and weight for each drum fed during each test. (Sampling of drums fed under these conditions is discussed in a later section.)

Operating Schedule

Consideration must be given to the operating schedule of the incinerator since it can have a significant impact on the test schedule and on the sampling methods. Most of the incinerators tested operated continuously, but there was one plant at which the specific type of waste to be tested was burned only once per week (which was the time period during which the feed tank was filled). Moreover, the entire contents of the feed tank were incinerated in less than 2 h. Thus, only one run could be conducted and it had to be completed within about 1 h, beginning very shortly after the unit was started up and had reached steady state conditions. It would not have been possible to conduct stack testing (Modified Method 5), including both traverses of the stack, within that period using only one sampling train. Thus, two trains were used simultaneously. As this particular sampling situation illustrates, the operating schedule of the incinerator can dictate changes in the normal testing and sampling requirements.

Design Considerations

Trial burn tests typically are intended to assess performance of the unit under conditions that are at or near design conditions. For example, the usual objective is to test the unit at the design heat input rate. In this case, the waste feedrates necessary to achieve that goal must be calculated based on heating value of the waste and then compared with actual feedrates just prior to and during the field testing. If data on the heating value of the wastes are not available prior to the tests, they must be estimated based on other known characteristics of the waste or on previous experience of the plant operators.

Another design aspect which should be investigated before starting the tests is the burner turndown ratio (i.e., design flowrate divided by actual flowrate). Results have shown that DRE can be adversely affected when burners operate at high turndown ratios. Liquid injection burners are designed to handle a certain liquid flowrate and usually have a manufacturer's recommendation regarding applicable turndown ratios. For example, a burner may be designed for a flow of 36 Lpm, with a maximum recommended turndown ratio of 3:1 (i.e., 12 Lpm). If, for some reason, the tests are conducted when feeding less than 12 Lpm, the high turndown ratio could adversely affect the burner atomization and resulting DRE. Such a situation did, in fact, occur during MRI tests at one plant, and we believe it probably caused the higher POHC emission rates and the resulting lower DREs.

The incorporation of design considerations, and in fact all process considerations, into the test plan is usually the responsibility of a "process monitor." The process monitor acts in the capacity of a project engineer for the trial burn. Ideally, the process monitor plays a

lead role in developing the sampling and analysis plan, oversees the actual field testing, and monitors the process data during the tests. The most critical process data taken by the process monitor are those which may later be specified as limits imposed in the operating permit; some of these are listed in Table II.

Most commonly, the process monitor must identify those parameters that must be monitored and ascertain prior to the test that instrumentation is available, adequate, and in good working order. It is very upsetting to realize after starting a test that an essential instrument does not appear to be operating properly and that operators have been aware for some time that the instrument is malfunctioning.

It is also essential to determine that an instrument is actually measuring what one thinks it is measuring; labels can be deceiving. For instance, a flowmeter may be located in a feedline, but with a downstream recirculation line back to the feed tank. Thus, it does not measure feedrate to the incinerator even though the label may imply that it does. Physical inspection and tracing of lines and instruments with operator assistance, before the tests, are highly recommended to avoid these situations and to ascertain exactly where each instrument is located and what it is measuring.

Allowable Process Variations

Prior to the start of any sampling, the process monitor must establish allowable process variations and predetermine those conditions under which all sampling activity must be stopped, and when it can be resumed.

One of the most common process limitations that must be established for any test is combustion chamber temperature. Limits may be set by examining previous operating data and by discussing the process with the plant operators, in order to determine temperature ranges that can reasonably be maintained (e.g., 1100°C ± 50°C). That information is then used to establish an "interruption" condition. For example, if the temperature is 25°C outside the "acceptable range" of 1050-1150°C for 15 consecutive minutes, sampling may be interrupted. Sampling would be restarted after the normal temperature (1100°C) was again established but with some consideration given to how much and how long the unit was outside the acceptable range.

Tight process limits were not the rule in the tests conducted by MRI for EPA because the intent was to assess performance under "normal" process operating practices, although desired temperature limits, etc., were made known to the operators. If these tests had been actual trial burns and were to result in certain operating limits being specified in the subsequent operating permit, then more specific limits, on a greater number of operating parameters, probably would have been established. In any case, such limits must be predetermined and known by the process monitor, sampling crew chief, and operators before the trial burn is started.

Table II. Monitored parameters.

Incinerator Operating Parameters

- Waste Feedrate[a]
- Combustion Temperature[a]
- Total Volumetric Airflow[a]
- Carbon Monoxide Concentration[a]
- Oxygen Concentration

Air Pollution Control System

- Scrubber Water Flow
- Scrubber ΔP

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[a] Monitoring after trial burn required by RCRA.

Not every circumstance that may require interruption in sampling can be anticipated, but usually the decision to interrupt is clear. The most frequent interruption occurrence is some type of electrical failure which causes an immediate shutdown. Occasionally, other unanticipated circumstances arise, and the process monitor must decide quickly whether the condition is likely to seriously affect the test results. If so, sampling must be interrupted. For this reason, the process monitor should be experienced in process operations and sampling methods.

Some process variations may be noted by the process monitor which are significant but have no predetermined limits and do not require interruption. The most vivid example of such a variation occurred during an MRI test involving solid waste fed to a rotary kiln. Different types of solids were being fed to the kiln, and the process monitor noted that the carbon monoxide and hydrocarbon levels increased each time a drum of solids was fed into the kiln, and that the increases were very large for one specific type of solid. These types of process observations can be very helpful in later evaluations of test results.

Field Sampling Experience

Field sampling experience and sampling methods are discussed in this section covering waste feed sampling, stack sampling, and sampling of other effluents.

Waste Feed Sampling

One of the major concerns in sampling waste feeds is waste variability and, consequently, the use of appropriate sampling techniques. Some field experience pertaining to waste feed variability and sampling is presented below for both liquid and solid waste feeds.

Liquid Waste Feeds. Tests conducted by MRI showed that liquid waste composition could be variable within any one run. Variability was observed even in cases in which the feed tank was equipped with a mixer or was continuously recirculated. The clearest indication of this variability was seen in process observations. That is, during very stable operation, temperatures would begin to rapidly increase (or decrease) and instrumentation would automatically adjust the liquid waste feedrate. Since the change seemed to occur without any indication on any other instruments that other parameters might be the cause, the only logical reason for the change appeared to be a change in the waste feed composition, indicating stratification in the waste feed tank.

Partly because of the type of process observation described above, it was considered necessary to sample the liquid waste feeds frequently during each run to form a composite sample. It was decided that subsamples could most practically be taken at 15-min intervals, and this was the procedure used at all plants tested. (Continuous sampling was not feasible for these feeds.)

One finding of the waste feed sampling experience is that great care must be used in sampling from the liquid organic waste feed lines. In taking each subsample, the sample tap must be opened long enough to drain out any liquid trapped in the sampling line so that the subsample taken is representative of the liquid flowing in the feed line. The draining and sampling from this tap must be done slowly and very carefully so as not to affect the flow of waste to the burner or to activate any automatic shutdown systems (e.g., low waste feed pressure). Proper safety precautions must be taken and appropriate personnel protective equipment used, depending on the characteristics of the waste being sampled.

At one plant it was not possible to sample directly from the waste feed line to the burner. Since the plant had a very small waste feed tank (~ 300 L capacity), each subsample was taken from a drain line in the bottom center of the tank, near the pump suction line located in the side of the tank near the bottom. This sampling point appeared to be satisfactory in the first run; but on subsequent runs, after additional waste was put into the feed tank, it became obvious that some of the subsamples had very high water content. The resulting conclusion was that the samples were probably not representative of the feed to the incinerator since the incinerator continued to operate well without any indication that the feed was indeed high in water content. Nonrepresentative samples were probably being obtained from the sampling point because of separation of water that collected in the bottom of the tank. Obviously this kind of situation must be avoided; waste feed samples should be taken from the waste feed line to the incinerator.

Solid Waste Feeds. No continuous solid feed streams were included in tests conducted by MRI, but some sites did involve drummed materials, fed intermittently. Drummed materials were usually solids or semisolids or, in some cases, liquids alone or multiphase liquids and solids. Solids also included anything from actual solids to glue-like material. As a result of this mix of wastes, it was necessary to employ many different drum sampling methods.

An attempt was made to sample every individual drum; but when several drums contained very similar or even identical waste, the samples were composited. Compositing of samples is reasonably easy to do if each drum can be sampled as it is fed to the incinerator. At one site, however, that was not feasible so all drums were sampled before testing. A record was kept of the drums fed to the incinerator during the actual test period, and samples from those drums were composited, as appropriate, after conclusion of the testing. The sampling itself involved 300 drums, so the task was not nearly as simple as it sounds.

Formation of the composite samples was usually done by taking approximately equal amounts from each drum (for drums of the same type of waste). Even if the amounts were exactly equal, this procedure would not be strictly correct if the drums were not of equal weight. However, because of the nature of most of the drummed wastes and their large number, an exact weighing and proportioning of the subsamples into a composite sample would have been impractical, if not impossible.

As mentioned earlier, the drummed wastes were highly variable and required use of different solids sampling methods (Trier, Coliwasa, grain thief). Some types of drummed waste were not amenable to sampling by any of these techniques. Consequently, it was necessary to modify the sampling methods to obtain the best samples possible in a reasonable amount of time, considering the large number of drums to be sampled.

One conclusion reached as a result of this sampling activity was that the Coliwasa should be modified because it was difficult to use, did not seal properly in many cases, and obtained too large a sample. MRI therefore developed a modified Coliwasa that eliminated the above problems (see Figure 1). This modified Coliwasa provides a positive seal at the bottom by use of a ball valve; it provides a smaller sample size; and it is still usable through the bunghole in the lid of a drum.

Again, proper safety procedures and personnel protective equipment must be used whenever drum sampling is conducted. One special precaution must be noted: "bulging" drums can indicate pressure buildup. When faced with this problem, MRI always deferred to the plant operators for opening of the drums.

Stack Effluent Sampling

The preceding sections of this paper have addressed waste feed sampling and measurement of waste feedrates, both of which are necessary for determination of DRE for POHCs and for determination of HCl removal efficiency. Equally important, and probably the most difficult, is the sampling of stack effluent, which is also necessary for determining DRE, and HCl and particulate emissions. Much of MRI's field sampling experience pertains to stack effluent sampling. Those items summarized in the following sections are only some of the items important in stack effluent sampling. They represent considerations which our field experience indicates could be especially troublesome or which could benefit others through additional explanation and discussion.

Cyclonic Flow Considerations. One of the first steps prescribed for stack sampling by Method 5 (M5) is a preliminary check for cyclonic flow. That procedure was carried out at all test sites, and significant cyclonic flow was found to exist at the stack sampling location for two of the sites. Cyclonic flow might have been anticipated at one site since the forced draft fans directed the air flow tangentially into the combustion chamber. At the other site, however, there was no reason evident for cyclonic flow. In both cases, the flow vector angle exceeded the limit of 10° specified in EPA Method 1. Flow straighteners were fabricated and inserted in the stack several diameters upstream of the sampling location to eliminate the cyclonic flow problem before the tests were performed.

This experience shows that cyclonic flow may exist in a stack even when there is no obvious reason to expect it. The problem can be eliminated by installation of flow straighteners; but even where it is possible to do so, this step can cause considerable delay. Usually the

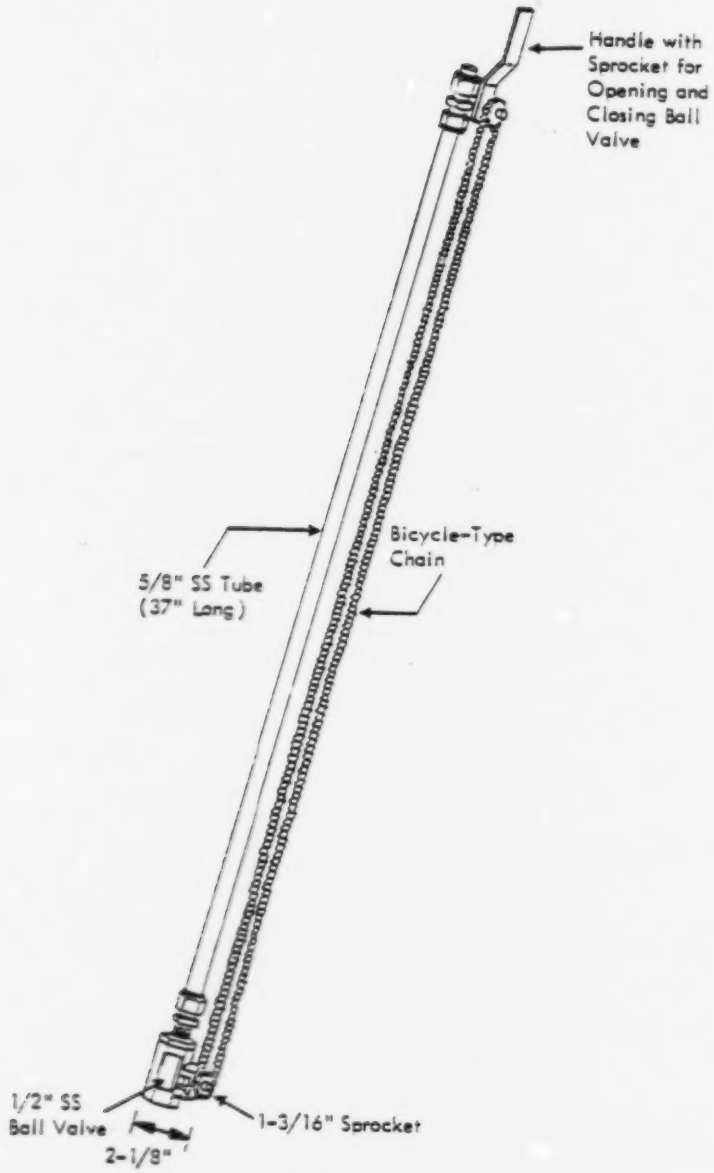

Figure 1. Diagram of Modified Coliwasa

check for cyclonic flow can be done only just prior to the start of testing. If cyclonic flow is found to exceed the EPA limit, a flow straightener specifically designed, fabricated, and installed, was found to be an effective means of correcting the problem. This procedure will likely require shut-off and cool-down of the incinerator. It was fortunate in the two instances cited that the work could be accomplished with a delay of only one day. However, a delay of several days might be necessary in other situations. Obviously, if there is reason to believe that the flow may be cyclonic, a flow straightener should be installed in advance of the tests.

POHC Sampling Methods. There are two categories of POHCs: semivolatile and volatile. In general, the volatile POHCs have a boiling point below 135°C. But in practical terms, the real difference between the two categories is that different sampling and analytical methods are required.

Sampling for semivolatile POHCs requires use of an MM5 train containing an XAD resin trap. Sampling for volatile POHCs requires use of a gas bag or a volatile organic sampling train (VOST), or both. Many POHCs (RCRA Appendix VIII compounds) can be sampled with the above methods, but some require special methods (e.g., formaldehyde). Therefore, it is necessary to know what POHCs must be quantified and to examine available information (especially Reference 1) to identify appropriate sampling methods. Once that has been done, one must estimate the concentration of each POHC in the stack effluent to determine the detection limit required and then select the sampling methodology, sample quantities, and analysis methodology appropriate to that detection limit. These detection limit considerations are discussed in the next section for semivolatile and volatile POHCs.

Detection Limit Considerations.

Semivolatile POHCs--Tests conducted by MRI have shown that the quantity of each POHC collected in an MM5 train should be a minimum of 1 μg to be detectable in the subsequent gas chromatography/mass spectrometry (GC/MS) analysis of the combined extract of the MM5 train components. If an incinerator burns a waste containing only 100 μg/g (100 ppm) of a POHC and is achieving a DRE of exactly 99.99%, the resulting POHC concentration in the stack effluent would be about 1 $\mu g/m^3$ (1 ng/L). On this basis, sampling 1 m^3 of stack gas would provide only the minimum quantity of the POHC necessary to meet the detection limit.

MM5 sampling rates average about 1 m^3/h, so a normal sampling time of 2 to 3 h should provide enough of the POHC (2 to 3 μg) to be above the detection limit (1 μg) and therefore demonstrate that the DRE of 99.99% is achieved.

If the concentration of the POHC in the stack effluent is higher than 1 $\mu g/m^3$, because of a DRE below 99.99% or because of a much higher concentration in the waste feed, the extract can be diluted for analysis. In the case of volatile POHCs, samples cannot be diluted and

reanalyzed because the constituents are thermally desorbed rather than extracted. Closer control of the volume of gas sampled using VOST, or alternative methods, may be necessary as discussed below.

Volatile POHCs--In most of the tests conducted by MRI, both VOST and gas bags were used for sampling volatile POHCs. Both can achieve acceptable detection limits if a portion of the gas bag sample (~ 5 L) is first passed through a Tenax trap (VOST trap) rather than a small amount being injected directly into the GC/MS analysis system.

Operating procedure for the VOST requires drawing 20 L of stack gas through each pair of traps. If the gas contains 1 ng/L of a POHC (as discussed above) the amount contained on any one pair of traps (or on one of the two traps) would be 20 ng, which is well above the detection limit of about 2 ng. However, if the concentration in the waste feed is much higher, say 100,000 μg/g (10%), the resulting POHC concentration in the stack effluent would be 1,000 ng/L when the incinerator is achieving a DRE of exactly 99.99%. If VOST is used in this case and operated at the same sampling rate and sampling time as above, the amount of POHC caught on any one pair of traps would be 20,000 ng. Since the traps are thermally desorbed, this entire quantity would enter the GC/MS and would very likely saturate the MS. When this saturation occurs, it is difficult or impossible to quantitate the amount of POHC; thus, the DRE could not be determined.

The best alternative for quantifying high concentrations of volatile POHCs may be to sample with gas bags or gas bulbs (glass) and to analyze much smaller samples (e.g., 1 mL) by direct injection into the GC or GC/MS.

The real problem in determining DRE for volatile POHCs occurs in cases in which there is more than one POHC, with some present at high concentration and others at low concentration. Since neither VOST nor gas bags alone may adequately quantitate both low and high concentration POHCs, both sampling methods could be necessary.

MRI's experience has been that POHCs present at high concentrations in waste feeds showed very high DRE, so sampling volatile POHCs by VOST alone would have been sufficient. However, one cannot always assume that VOST would be adequate. For a POHC present at high concentration in a waste feed, it is essential to be able to quantitate a high concentration in the stack effluent in order to determine if the desired DRE of 99.99% was or was not being achieved. Therefore, if more than one volatile POHC is present, and depending on their respective concentrations in the waste, one must determine which sampling method(s) should be used.

In summary, it is necessary to estimate the concentration of each POHC in the stack effluent based on the assumption that 99.99% DRE will be achieved (which must be demonstrated). Each of these estimated concentrations provides a guide for the detection levels required in the sampling and analysis methods. Appropriate methods and the required sampling times or sample volumes can then be selected.

It is preferable to use sampling and analysis methods whose detection limits are much better than the quantities actually expected to be present in the samples. Another factor related to detection limits that can be very important is the level of the blanks. This factor is discussed in the next section.

Blank Requirement Considerations. Blanks are certain materials or reagents used in the sampling methods. They are treated the same as samples, except that they are not used in collection of actual samples. Taking blank samples is an extremely important part of the sampling and analysis activities, both for quality assurance purposes and for evaluating results. In conducting particulate sampling (Method 5), it is normal to take probe rinse reagent blanks and filter blanks in order to properly correct the final particulate results. Blanks are perhaps even more important for quantifying POHCs.

The discussion in this section is divided into three parts. The first part discusses MM5 blanks, for semivolatile POHCs. The second and third parts discuss VOST blanks and gas bag blanks, respectively, for volatile POHCs.

Modified Method 5 Blanks--MM5 is used for quantifying particulate emissions, HCl emissions, and semivolatile POHCs, all as part of a single sampling train. As a result, the probe rinse reagent blanks and filter blanks serve a dual purpose, since they are used as blanks for particulate emissions and for semivolatile POHCs. The MM5 train includes an XAD resin trap, so a blank XAD trap is also required. Like the MM5 samples themselves, all three of the above MM5 component blanks must be extracted and the extracts combined and analyzed. The analysis result for the blanks can then be used to correct the sample results if the amount of POHCs in the samples is "significantly" greater than any amounts found in the blanks.

In previous trial burn tests, MRI blank corrected the results if the sample amount was more than three times the blank. If not, the entire sample amount was used and expressed as a "less than" value, which meant that the DRE calculated therefrom had to be expressed as a "greater than" value. This occurred frequently when both the samples and the blanks were below the detection limit. In some cases, but very infrequently, both the sample value and the blank value were high, resulting in a "greater than" value for DRE which was below 99.99% (e.g., > 99.98%). This result is not acceptable, however, since it does not show that the desired DRE of 99.99% was achieved.

VOST Blanks--Procedures used by MRI required two pairs of VOST blanks for each run (three runs per test site). For each run, one pair of traps served as a trip blank and one pair as a field blank. The only difference in these blanks was that trip blanks were never opened in the field, whereas the field blanks were taken up on the stack and opened to the ambient air for about the same period of time that an actual sample pair was open to the ambient air (i.e., when inserting and removing a pair of traps from the VOST).

Results obtained at each test site showed no statistically significant difference between the trip blanks and the field blanks, indicating that field blanks did not become "contaminated" due to their exposure in the field. It was then possible to calculate a mean and standard deviation for the six pairs of blanks (i.e., three pairs of trip blanks and three pairs of field blanks).

Results for the actual VOST sample pairs from each run were averaged (three pairs per run). This average value was then blank corrected using the mean value calculated for the blanks, if the average for the three sample pairs was higher than the following:

(blank mean value) + (3 times the standard deviation of the blanks)

Samples cannot be blank corrected when the above criteria are not met. Several VOST samples could not be blank corrected because both the samples and the blanks were below the detection limit. Consequently, the DRE had to be reported as a "greater than" value.

In the initial tests in which VOST was used in the field, the VOST blanks were frequently quite high, sometimes equaling or exceeding amounts in the actual samples. This created a serious problem and led to extensive cleanup procedures, which are discussed in the section below entitled "VOST Cleanup Procedures."

Gas Bag Blanks--Both VOST and gas bags were used at most of the sites tested by MRI. Tedlar gas bags were used to collect stack gas samples continuously over a 1- to 2-h period during each test. In addition, as a blank for each test, another Tedlar bag was filled with prepure nitrogen and inserted in the same, or an identical, sampling box as the sample bag and taken up to the sampling platform. After each test, the sample bags and the blank bags were returned to MRI for analysis.

Results from the blank bags were extremely important since in many cases analysis showed that they contained concentrations of some POHCs that were greater than the concentrations in the sample bags. This problem was investigated, including bag preparation procedures and methods of transporting and protecting the samples, but no definite cause or method of prevention was ever identified. In fact, these types of problems were part of the reason that the VOST system was originally developed. Results of the sampling experience certainly indicated that bag contamination can be a problem.

In most of the tests conducted by MRI, gas bags (and VOST) were used for sampling volatile POHCs. Glass bulbs could be used instead of gas bags to quantitate high concentrations of volatile POHCs, and might be better than gas bags if blank levels are lower in the glass bulbs. However, even if the blank levels are lower, glass bulbs have the disadvantage that they have a relatively small volume and therefore usually represent only short-term grab samples.

VOST Cleanup Procedures. Preparations for field testing include many cleanup procedures for sampling equipment and sample containers. Analytical results have shown that the cleanup procedures for the VOST traps are especially important and that each trap must be checked prior to field sampling to confirm that each meets required low levels of contamination.

One of the last, and most important, steps in the cleanup is the purged heating of every trap and a flame ionization detector (FID) analysis of the effluent purge gas from each trap. No trap is considered clean and ready for shipment to the test site unless the FID analysis shows that the effluent purge gas contains less than 5 ppb of total hydrocarbons (based on propane as the FID calibration gas). After MRI adopted the rigorous cleanup procedures, test results confirmed that POHC levels in the blanks were low, and that the criterion of 5 ppb total hydrocarbons served as a good basis for checking each trap prior to use.

Sampling Other Effluent Streams

Other effluent streams sampled in many of the tests were scrubber liquids and ash. Scrubber liquid sampling presented no special problems and was usually done by taking grab samples from sampling taps in the piping. However, the test results for the scrubber samples revealed an unexpected problem, which is discussed below.

Scrubber Liquids Sampling. Most of the scrubber makeup waters were chlorinated water (e.g., municipal water supply) and therefore contained trihalomethanes (e.g., chloroform). In passing through the scrubbers, these trihalomethanes were stripped from the water by the stack gases. As a consequence, they were then detected in the stack gases and reported as PICs or as undestroyed POHCs. Where any of these trihalomethanes had been designated as a POHC, their presence in the stack gas had an impact on the calculated DRE.

Material balance calculations usually showed that most or all of the trihalomethanes in the stack gas could be accounted for by the scrubber makeup water. This finding clearly demonstrates the extremely low concentrations of compounds (POHCs) that can be detected by the stack sampling methods, and how other factors can have a significant impact on the resulting DREs. It also shows why it may be advisable to sample and analyze scrubber water samples, even though such data are not directly entered into the calculation of DRE. Wherever possible, it would be preferable not to select as POHCs those compounds that may also be present in the scrubber makeup water.

Ash Sampling. As mentioned, the actual sampling of scrubber water did not present any special problems. Sampling of ash, on the other hand, did. Three types of ash sampling situations were encountered in this program which made it difficult to obtain representative samples. The first situation was one in which ash accumulates in the combustion chamber and can be sampled only after shutdown. This situation requires

that all ash be cleaned out prior to the test. The test wastes must then be fired until the unit is shut down after the test so that the samples can be taken. Even then, it may be difficult to obtain samples that are representative. The second situation involved the ash that remains in barrels that pass intact through a combustion chamber. As with sampling solid wastes in drums, the ash in drums can be very difficult to sample representatively. The third, and probably most difficult, situation was sampling of ash that is sluiced out with water. In this situation, the representativeness of the ash samples is always uncertain.

Conclusion

A long list of complex factors must be considered in conducting a trial burn. Consideration of all these factors is necessary in order to avoid the serious problems that can occur if any of them are ignored or overlooked.

The preceding discussions have used actual field sampling experience at hazardous waste incinerators to identify and explain some of the more important or troublesome aspects of trial burn sampling activity. Many of these aspects are mentioned in available sampling and analysis methods manuals,[1,2,3] but they may not be clearly explained or their importance immediately obvious. Other aspects are not covered in the available manuals and are based on MRI's experience and the results from the trial burns.

It is hoped that these observations on our field experience in conducting trial burns and utilizing the sampling methods will aid others who may be planning trial burns or who may be performing sampling and analysis activity.

References

1. Harris, J. C., et al., "Sampling and Analysis Methods for Hazardous Waste Combustion," 1st ed., Arthur D. Little, Inc., report for the U.S. Environmental Protection Agency, EPA Contract No. 68-02-3111 (Feb. 1983).

2. U.S. Environmental Protection Agency, "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846, 2nd ed., (July 1982).

3. U.S. Environmental Protection Agency, Office of Solid Waste and MITRE Corporation, "Guidance Manual for Hazardous Waste Incinerator Permits," (Mar. 1983).